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Process for producing pitches from coal tars and distillates thereof by oxidative thermal treatment

The invention relates to a process for producing pitches, in particular those suitable for use as carbon precursors, from coal tars and distillates thereof, through a sequential and combined operation in three steps:

1.- Reaction: Oxidative thermal treatment under mild conditions of pressure and temperature (<400° C, <10 bar g, residence time in the range of 2-10 seconds, and preferably 350-400° C, 5-10 bar g, 6-10 seconds), using air, oxygen, low-oxygen air or mixtures thereof as reagents.

2.- Thermal treatment under inert atmosphere (340-400° C, <10 bar g, residence time in the range of 3-10 hours, and preferably 370-400° C, atmospheric pressure, 4-6 hours) for stabilization of the reaction product.

3.- Fractional distillation (preferably in vacuum or by stripping with steam or inert gas) in order to adjust, according to the desired application, the softening point of the pitch or carbonaceous precursor.

Background of the invention

Pitches are mostly produced by distillation of coal tar. The tar, once dehydrated and after removal of a first light fraction of BTX (<5%), gives rise to the following fractions according to the different distillation cuts:

• Naphthalene oil fraction. Within a distillation range of less than 260° C and with a naphthalene content greater than 50%, it represents approximately 20% of the parent tar and is used for the recovery of naphthalene of high commercial value as well as for the production of technical oils.

• Anthracene oil fraction. A complex mixture of polycyclic aromatic hydrocarbons within a distillation range of 260-400° C mainly formed by anthracene, phenanthrene, fluoranthene, pyrene and carbazole. It represents approximately 30% of the parent tar, an d is a directly marketable product for the production of carbon black in strong competition with various petroleum residues. Also would be of commercial interest the conversion into pitch of the major portion of this fraction.

• Pitch. The largest product obtained from tar distillation. It is a black solid with a softening point of about 30-250° C, characterized by its content of substances insoluble in certain solvents such as toluene and quinoline. It is a complex mixture of polycyclic aromatic hydrocarbons with three or more condensed aromatic rings

and represents approximately 50% of the parent tar. It is one of the raw materials employed in the manufacture of electrodes for aluminium and graphite industries.

Since the method for producing pitch consists only in the separation of oils until adjustment of the softening point of the pitch pre-existing in tar, its production can be regarded accordingly as a pure physical operation. Therefore, the quality of pitches obtained by prior art techniques is ruled by the quality of the tars present in the production process.

The characteristic fact that coal tar is a byproduct from coke batteries makes this raw material a highly inconsistent product, and this drawback is only compensable through the formulation of suitable tar blends. In any event, all types of tars and, consequently, pitches obtained thereby, have solid particles in suspension (primary and secondary QI, and carry-over), besides different types of metallic sludge identifiable by its ashes content. Both pollutants prejudice pitch quality and/or decrease its potential application in advanced carbon materials.

Anthracene oil is obtained along distillation of coal tar and is characterized by its distillation range, which is comprised from about 260° C until the corresponding temperature for adjusting the softening point of the pitch obtained as a final product (generally 400-410° C). Anthracene oil is mostly constituted by aromatic hydrocarbons of 2-4 benzene rings and the corresponding heterocyclics with O, N and S, phenanthrene, anthracene, fluoranthene, carbazole and pyrene being the main components. High aromaticity of anthracene oil and the characteristic of being a distilled product and entirely distillable in its whole range, convert this product into a raw material of highly consistent quality, what suggests the possibility of more refined uses.

Many of the aromatic hydrocarbons present in anthracene oil and some heteroaromatic ones are transformed into anisotropic and graphitizable carbonaceous materials by means of slow thermal treatment up to 1000° C in a closed vessel duly pressurized for avoiding evaporation. Thermal treatment up to a lower temperature would halt transformation at an intermediate stage –the pitch– although with a low yield thereof. The process consists of a dehydrogenating aromatic condensation which is generated by radical pathways. Said intermediate step for producing pitch still proceeds under excessively high temperatures and low conversion rates for proper application at industrial level. All this suggests the possibility of inducing aromatic condensation by means of catalytic reactions that promote generation of radicals, and their condensation and

dehydrogenation at lower temperatures with a higher yield. Among the possible inductors for this type of reactions, the catalysts of Friedel-Craft (BF_3/HF, $AlCl_3$) and sulfur are well known. For the quality of the final products or by reason of operation costs and residues/byproducts generated such catalysts are not advisable, thus proposing for this case, and constituting an objective of the present invention, the use of oxygen, air, low-oxygen air or mixtures thereof in the reactions.

The treatment with air of tars and pitches as well as composite materials, self-syntherizable mesophase and fibers has been used actually for different purposes such as the increase of molecular weight and softening point of pitches and tars, the avoidance of swelling during carbonization in composite carbon/carbon materials and self-syntherizable mesophase, and the thermal stabilization of fibers before carbonization.

Patent EP-A-0167046 discloses the production of a pitch with low content in solids by means of oxidation with air or oxygen of a distillation fraction selected from coal tar or a heavy oil derived thereof, while heated at preferred temperatures of 315-385° C, though the possibility of operating at a lower temperature (149° C) is mentioned, until obtaining a desired intermediate product. This intermediate product is then submitted to distillation by stripping with steam or an inert gas, although said distillation could be avoided by using higher temperatures in the oxidation phase. The result is an impregnating pitch especially useful in the manufacture of electrodes.

The possibility of introducing an intermediate thermal treatment in order to improve both the pitch quality (in rheological terms and fixed carbon) and final yielding is not regarded in said patent. The pressure conditions or the time required for the processing steps are also not mentioned in the patent.

Description of the invention

The process according to the invention, in comparison with the prior art, starts with a wider range of raw materials, including petrochemical aromatic fractions. Pitches obtained in accordance with the invention, when compared with those of the prior art, present a higher intrinsic quality and improved properties in relation to health (carcinogenesis) and environment.

The reaction of anthracene oil with the oxygen present in the air at temperatures lower than 400° C and preferably higher than 350° C, produces a molecular condensation

through mechanisms that, in view of the reactivity of the main components of anthracene oil, appear to be similar to those present when sulfur is used as catalyst.

There has been observed that parameters such as temperature, residence time, gas flow (air/oxygen) and charge and pressure of the reactor, have an effect on the reaction course by favoring or inhibiting the aromatic condensation reactions, which are critical for the formation of compatible molecular structures able to promote aromatic condensation reactions instead of polymerization and cross-linking reactions. An additional thermal treatment under inert atmosphere enables to increase planarity of molecules and to stabilize the reaction product, in the sense of filtering possible side reactions, which further promotes its wettability, increases its graphitizability and generally improves the reaction yield.

Pitches produced according to the present invention exhibit a substantial reduction in carcinogenic components due to the limited presence thereof in anthracene oil and their reaction through the proposed conditions of operation. At the same time, the performance of fractional distillation in vacuum, together with the molecular weight distribution achieved by means of the selected conditions of operation, produce a pitch with a reduced volatility what means a substantial environmental benefit.

The reaction of anthracene oil with air generates only water as byproduct/effluent (slightly polluted with ammonia and equivalent in composition to the ammoniacal waters obtained during the tar distillation process) and a gaseous current that comprises low-oxygen air, CO and CO_2. Since the pitch or carbonaceous material is free from solid particles and metallic sludge, the resulting product will not contain such stuff.

According to the selected conditions of reaction, the resulting pitch can generate cokes which when observed under optical microscopy with polarized light, can appear as 100% anisotropic or 100% isotropic, depending on the properties of the pitch receiving interest.

In view of the advantageous characteristics of the pitches obtained by the process of the invention, such pitches are suitable for applications belonging to the field of carbon precursors and in particular are useful in the manufacture of electrodes for aluminium industry, graphite electrodes and synthetic graphite in general, binders for refractory industry, waterproof materials and electrometallurgical paste.

Due to the low selectivity of the reaction, the unreacted anthracene oil may be directly put in commerce, in accordance with the usual applications of said raw material obtained by tar distillation. Additionally, the increase of anthracene/phenanthrene concentration, as a consequence of these being poorly reactive components, would provoke that said fraction could promote the actual interest in the manufacture of anthracene paste.

During the process, three phenomenological situations derived from side reactions to avoid are generated:

1. Formation of cross-linked structures/gums.
2. Generation of solid particles.
3. Generation of high molecular weight structures.

The conditions for the process were determined with the purpose of avoiding the above-mentioned side reactions, while maximizing yield, economy and safety of the process. For that reason, the following parameters of operation were selected:

- Temperature: 250-400° C, preferably 350-400° C.
- Pressure: 5-10 bar g.
- Specific airflow (21% O_2): 0.1-0.25 kg/kg of anthracene oil.
- Residence time during reaction: 2-10 seconds, preferably 6-10 seconds.
- Conversion in a single step: ≤40%. By means of successive transformation steps, net yields of 60% or more can be achieved.
- Thermal treatment under inert atmosphere: 340-400° C, 3-10 hours, 0-10 bar g, preferably 370-400° C, atmospheric pressure and 4-6 hours.
- Distillation up to softening point: According to the application. In the range of 85-250° C Mettler for conventional applications.

In accordance with the invention, the process is carried out through sequential combined application in three steps:

- Oxidative thermal treatment (reaction)
- Thermal treatment under inert atmosphere (stabilization)
- Fractional distillation in vacuum (adjustment of softening point and depletion of volatile components).

Pitch thus obtained, in comparison with that produced by standard processes, i.e. EP-A-0167046, gives yields of about 50%. It is a pitch usable in multiple applications and

has improved properties in relation to health (carcinogenic components content) and environment (volatile components content).

Description of the drawings

For carrying out the process according to the invention, it was used, though in no binding or limitative fashion, the pilot plant which scheme is illustrated in annexed Figure 1, and in which the respective numerical references designate:

1. Reactor
2. Recirculation pumps
3. Reagent dosing system (air/oxygen)
4. Static mixer
5. Oxygen analyzer
6. Thermal treatment vessel
7. Distillation column for softening point adjustment.
8. Pressure regulator
9. Temperature regulators
10. Heating systems
11. Venting
12. Anthracene oil inlet
13. Purge
14. Recirculation of unreacted anthracene oil
15. Pitch outlet

Examples

The following examples, given without limitative character, relate to embodiments of the invention.

As preferable raw material it is used anthracene oil arising from coal tar distillation with the following average characteristics (non-limitative aspect):

Raw material: Anthracene oil	
Origin	Distillation of high temperature tar
Distillation range (BS144)	> 260° C
Density (ASTM D1298)	> 1.120 g/cm^3 (20° C)
Ashes (ASTM D482)	< 0.02%
Toluene insolubles (BS144)	< 0.1%
C/H atomic ratio (ASTM D5291)	> 1.30

According to the advantageous characteristics of the invention, different carbochemical fractions can be used by means of widening or narrowing the proposed distillation range, with no inconvenient for the quality of the product. The sole substantial variation to be obtained will be that derived from a higher or lower yield in the process.

Where non-carbochemical oils or components with a high content of heteroatoms, and/or components with high content of naphthenic structures and lateral chains are used, the reaction must be conducted under vigilance in order to avoid the formation of gums and cross-linked structures. It is recommendable to maximize the temperature and reduce the conversion to a single step.

Example 1

In the above-described pilot plant was processed an anthracene oil sample under the following conditions:

- Temperature: 300° C
- Residence time: 6 seconds
- Specific airflow: 60 Nl/h air per kg of oil
- Pressure: 5 bar g
- Thermal treatment: 400° C, 5 hours, 10 bar g
- Distillation: Adjustment to softening point 90° C Mettler.

There was obtained a pitch with the following characteristics, in comparison with a standard impregnating pitch, and the net yield in pitch was 55%:

Parameter	Units	Example 1	Standard pitch
Softening point (ASTM D3104)	°C, Mettler	90	90
Flash point (ASTM D92)	°C, COC	274	250-270
Toluene insolubles (ISO 6376)	%	29.5	15.0
Quinoline insolubles (ASTM D2318)	%	1.0	0.8
Beta-resin	%	28.5	14.2
Fixed carbon (CRDG-B10)	%, Sers	44.7	40.1
Filtration rate	g, 80 min	43.3 (6 min)	15-20
Ashes (ASTM D2415)	%	<0.01	0.1

It is observable the substantial increase in the rheological properties, measured through filtration rate and increments in beta-resin and fixed carbon, of the resulting pitch.

Example 2

In the above-described pilot plant was processed an anthracene oil sample under the following conditions:

- Temperature: 350° C
- Residence time: 4 seconds
- Specific airflow: 60 Nl/h air per kg of anthracene oil
- Pressure: 5 bar g
- Thermal treatment: 400° C, 5 hours, 10 bar g
- Distillation: Adjustment to softening point 90° C Mettler.

There was obtained a pitch with the following characteristics, in comparison with a standard impregnating pitch, and the net yield in pitch was 38%:

Parameter	Units	Example 2	Standard pitch
Softening point (ASTM D3104)	°C, Mettler	90	90
Flash point (ASTM D92)	°C, COC	276	250-270
Toluene insolubles (ISO 6376)	%	25.3	15.0
Quinoline insolubles (ASTM D2318)	%	0.4	0.8
Beta-resin	%	24.9	14.2
Fixed carbon (CRDG-B10)	%, Sers	43.1	40.1
Filtration rate	g, 80 min	59 (6 min)	15-20
Ashes (ASTM D2415)	%	<0.01	0.1

It is observable that the control of the conversion and a higher reaction temperature (in regard to Example 1) provide a product with improved filtration rate and lower generation of quinoline insolubles, as a consequence of a lower generation of cross-linked structures, which are high molecular weight compounds, and since the process is carried out in less time, a lower generation of solids.

Example 3

In the above-described pilot plant was processed an anthracene oil sample under the following conditions:

- Temperature: 350° C
- Residence time: 4 seconds
- Specific airflow: 60 Nl/h air per kg of anthracene oil
- Pressure: 5 bar g
- Thermal treatment: 400° C, 5 hours, 10 bar g
- Distillation: Adjustment to softening point 110° C, Mettler.

There was obtained a pitch with the following characteristics, in comparison with a standard impregnating pitch, and the net yield in pitch was 35%:

Parameter	Units	Example 3	Standard pitch
Softening point (ASTM D3104)	°C, Mettler	110	110
Volatiles (ASTM D2569)	% a 360° C	0.0	0.3
Toluene insolubles (ISO 6376)	%	29.2	29.0
Quinoline insolubles (ASTM D2318)	%	1.3	10.0
Beta-resin	%	27.9	19.0
Fixed carbon (CRDG-B10)	%, Sers	49.0	54.0
Wettability (CRDG SERS)	°C, Goutte	137	134
Ashes (ASTM D2415)	%	<0.01	0.1
B[a]P equiv.	g/kg, EPA	18	28

In this example the resulting pitch would be suitable for its application as a binder pitch for electrodes in aluminium industry. When a greater ratio of quinoline insolubles is required, it is possible to prepare blends with a carbochemical pitch with high insolubles content, in which case there would be obtained a pitch with improved beta-resin and fixed carbon (normalized to the insolubles level) parameters.

From the above-mentioned properties can be deducted the potential advantages of the process for generating carbon precursors with less content in carcinogen compounds (B[a]P equiv.) and lower environmental impact (absence of volatile components at 360° C).

Example 4

In the above-described pilot plant was processed an anthracene oil sample under the following conditions:

- Temperature: 350° C
- Residence time: 4 seconds
- Specific airflow: 60 Nl/h air per kg of anthracene oil
- Pressure: 5 bar g
- Thermal treatment: None
- Distillation: Adjustment to softening point 90° C Mettler.

There was obtained a pitch with the below characteristics, in comparison with a standard impregnating pitch, and the net yield in pitch was 35%. In the following table are also enclosed, with a further comparative purpose, the results for the sample of Example 2 as reference data showing efficacy of the intermediate thermal treatment recommended by the invention.

Parameter	Units	Example 2	Standard pitch	Example 4
Softening point (ASTM D3104)	°C, Mettler	90	90	90
Flash point (ASTM D92)	°C, COC	276	250-270	272
Toluene insolubles (ISO 6376)	%	25.3	15.0	23.8
Quinoline insolubles (ASTM D2318)	%	0.4	0.8	0.5
Beta-resin	%	24.9	14.2	23.3
Fixed carbon (CRDG-B10)	%, Sers	43.1	40.1	42.0
Filtration rate	g, 80 min	59 (6 min)	15-20	67 (55 min)
Ashes (ASTM D2415)	%	<0.01	0.1	<0.01

In this case can be observed how the performance of a stabilizing thermal treatment improves filtration rate (rheological properties). At the same time, there is verified the influence over beta-resin, fixed carbon and global yield of the thermal treatment.